

**Tuesday 22 January 2013 – Afternoon**

**A2 GCE CHEMISTRY B (SALTERS)**

**F335/01** Chemistry by Design

Candidates answer on the Question Paper.

**OCR supplied materials:**

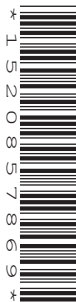
- *Data Sheet for Chemistry B (Salters)* (inserted)

**Other materials required:**

- Scientific calculator

**Duration: 2 hours**

**MODIFIED LANGUAGE**




Candidate forename		Candidate surname								
Centre number						Candidate number				

**INSTRUCTIONS TO CANDIDATES**

- The Insert will be found in the centre of this document.
- Write your name, centre number and candidate number in the boxes above. Please write clearly and in capital letters.
- Use black ink. HB pencil may be used for graphs and diagrams only.
- Answer **all** the questions.
- Read each question carefully. Make sure you know what you have to do before starting your answer.
- Write your answer to each question in the space provided. If additional space is required, you should use the lined page(s) at the end of this booklet. The question number(s) must be clearly shown.
- Do **not** write in the bar codes.

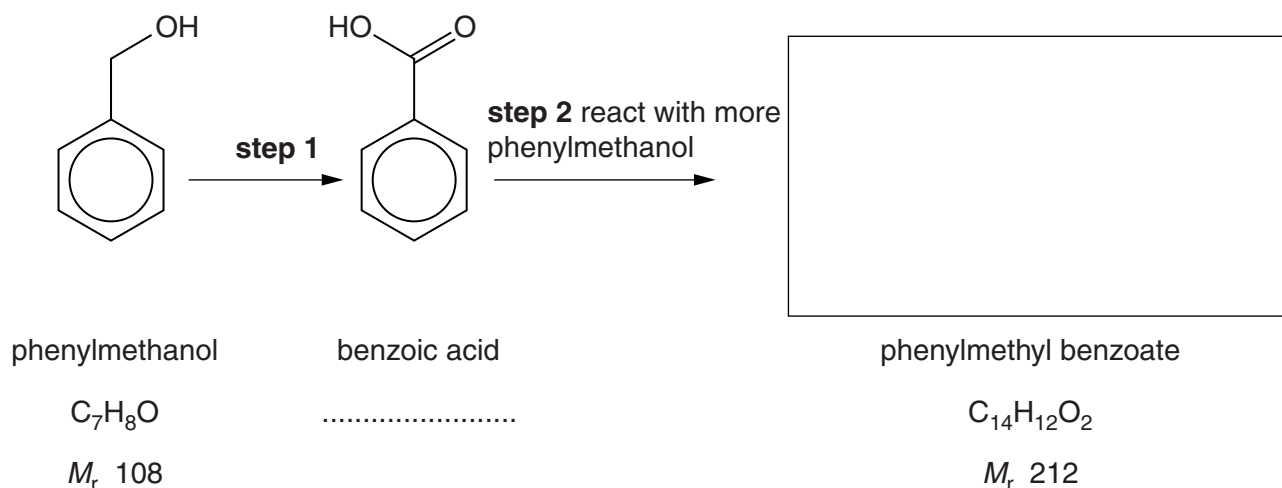
**INFORMATION FOR CANDIDATES**

- The number of marks is given in brackets [ ] at the end of each question or part question.
-  Where you see this icon you will be awarded marks for the quality of written communication in your answer.  
This means for example you should:
  - ensure that text is legible and that spelling, punctuation and grammar are accurate so that meaning is clear;
  - organise information clearly and coherently, using specialist vocabulary when appropriate.
- You may use a scientific calculator.
- A copy of the *Data Sheet for Chemistry B (Salters)* is provided as an insert with this question paper.
- You are advised to show all the steps in any calculations.
- The total number of marks for this paper is **120**.
- This document consists of **24** pages. Any blank pages are indicated.

Answer **all** the questions.

- 1 The ester phenylmethyl benzoate is used in food flavouring.

It can be synthesised in the laboratory from phenylmethanol using the reaction sequence below.



- (a) (i) Draw the skeletal formula for phenylmethyl benzoate in the box above. [1]
- (ii) Write the molecular formula for benzoic acid on the line below its name. [1]
- (iii) Give the other reagent and the conditions needed for **step 2**.

.....

..... [2]

- (iv) Use terms from the list below to classify the reactions in steps 1 and 2.

**addition    condensation    elimination    hydrolysis    substitution    oxidation    reduction**

step 1 .....

step 2 ..... [2]

- (b) (i) Calculate the atom economy of the formation of phenylmethyl benzoate from benzoic acid by the reaction in step 2.

atom economy = .....% [2]

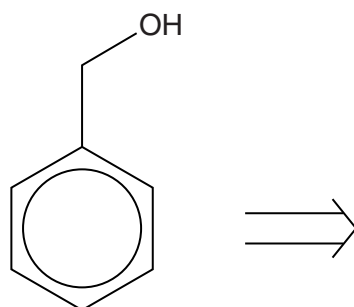
- (ii) Explain the importance to the environment of having industrial reactions with high atom economies.

.....  
 .....  
 ..... [1]

- (c) A synthesis for phenylmethanol can be devised using *retrosynthesis*.

The first step in the retrosynthetic analysis is to break the C–O bond. The electrons move to the synthon on which they would be more stable.

- (i) Illustrate the formation of the hydroxide ion and an organic cation by this method. Use a 'curly arrow' to show the breaking of the bond.



phenylmethanol (target molecule)

synthons

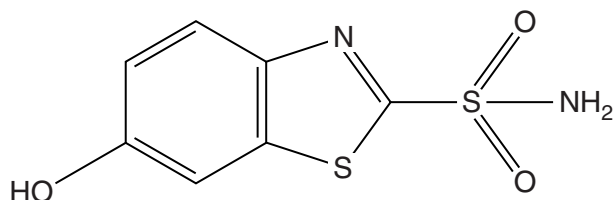
[2]

- (ii) Write the equation for the formation of phenylmethanol from two synthetic equivalents, one of which is a chloro compound.

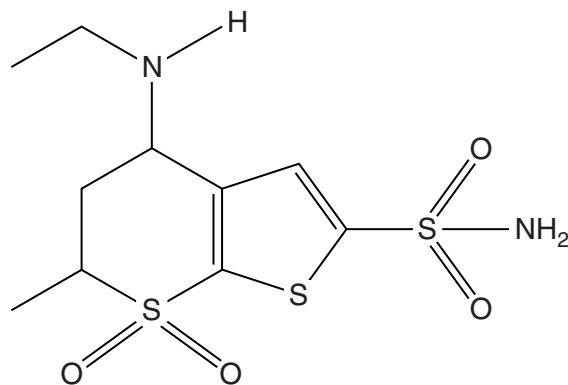
[2]

[Total: 13]

- 2 Compound **A** was known to be a treatment for an eye disease called glaucoma. *Dorzolamide* was designed by modifying the structure of compound **A** to make a more effective drug.



**compound A**



**dorzolamide**

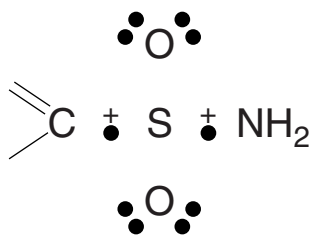
- (a) Both compound **A** and dorzolamide contain the same pharmacophore.

- (i) Explain the meaning of the term *pharmacophore*.

.....  
 .....  
 ..... [1]

- (ii) Circle the pharmacophore on the structure of **dorzolamide** above. [1]

- (b) (i) Complete the 'dot-and-cross' diagram for the electrons **around the sulfur atom** in the  $-\text{SO}_2\text{NH}_2$  group.



[1]

- (ii) Suggest, with reasons, the bond angles round the S atom in  $-\text{SO}_2\text{NH}_2$ .

.....  
 .....  
 .....  
 .....  
 .....  
 ..... [4]

- (c) Compound **A** is insoluble in water. This makes compound **A** less suitable to use in eye drops. Compound **A**, however, dissolves in a solution of pH 8.

- (i) Calculate the concentration of  $\text{OH}^-$  ions in a solution of pH 8.

$$K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

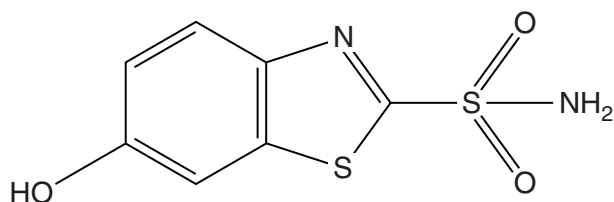
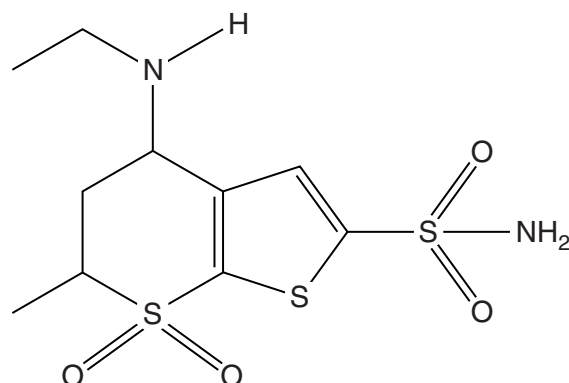
$$[\text{OH}^-] = \dots\dots\dots \text{ mol dm}^{-3} \quad [2]$$

- (ii) Explain, in terms of a functional group and its reaction, why compound **A** dissolves in a solution of pH 8.

.....  
.....  
.....  
.....  
.....  
..... [4]

- (iii) Suggest, with a reason, why a solution of pH 8 is not suitable for eye drops.

.....  
..... [1]

compound **A**

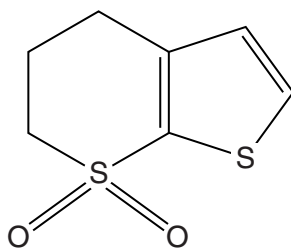
dorzolamide

- (d) Dorzolamide is more soluble in water than compound **A**. One reason is because it can form hydrogen bonds with water using the amine group that is **not** present in compound **A**.

Show the formation of **one** of these hydrogen bonds on the structure of **dorzolamide** above. Indicate relevant lone pairs and partial charges. [3]

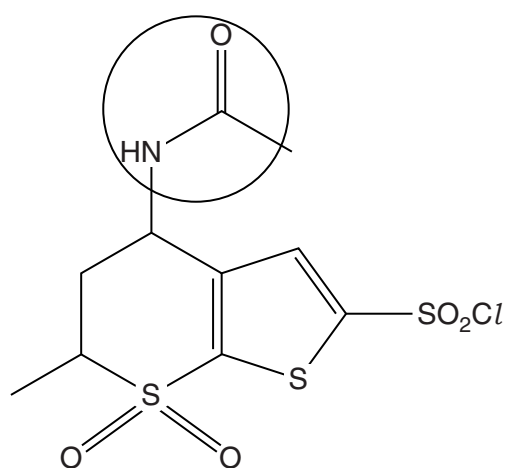
- (e) Dorzolamide has two chiral centres. Because these are on the same ring, they give rise to isomers that can be called *cis* and *trans*.

- Circle the two chiral carbon atoms on the structure of dorzolamide **above**.
- Draw wedge(s) and/or dotted line(s) on the diagram below. These should show a *trans* arrangement of groups around the chiral carbon atoms.

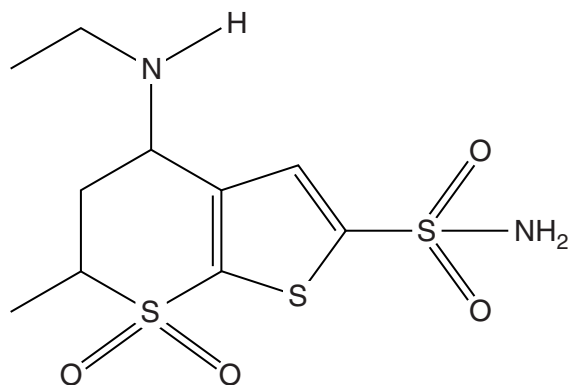
part of the structure of **dorzolamide**

[2]

- (f) Compound **B** is an intermediate in the synthesis of dorzolamide.



**compound B**



**dorzolamide**

- (i) Name the functional group that is circled in compound **B**.

..... [1]

- (ii) The group  $-\text{SO}_2\text{Cl}$  has some similar reactions to  $-\text{COCl}$ .

Suggest a reagent that could be used to convert  $-\text{SO}_2\text{Cl}$  to  $-\text{SO}_2\text{NH}_2$ .

..... [1]

- (g) Dorzolamide is an inhibitor of an enzyme that catalyses the reaction of carbon dioxide with water to form hydrogencarbonate ions.

- (i) Write an equation for this equilibrium reaction between carbon dioxide and water.

[1]

- (ii) Inhibitors slow down the rate of an enzyme-catalysed reaction.

Explain how inhibitors do this.

.....  
 .....  
 .....  
 ..... [2]

[Total: 24]

3 Calcium nitrate(V),  $\text{Ca}(\text{NO}_3)_2$ , is used as a fertiliser.

(a) (i) Write the full electron configuration for a calcium **atom**, in terms of s and p electrons.

..... [1]

(ii) Give the charge on the calcium ion and indicate how this charge is related to the position of calcium in the Periodic Table.

.....

..... [1]

(iii) Write the equation representing the **second** ionisation enthalpy of calcium.

Explain why the second ionisation enthalpy is smaller than the third ionisation enthalpy of calcium.

equation, showing state symbols:

explanation: .....

.....

.....

.....

..... [3]

(b) What does the 'V' in the name nitrate(V) indicate?

.....

..... [1]

(c) Calcium nitrate(V),  $\text{Ca}(\text{NO}_3)_2$ , can be made by reacting calcium hydroxide with nitric acid,  $\text{HNO}_3$ .

(i) Write an equation for this reaction.

[1]

(ii) Explain why calcium nitrate(V) is used as a fertiliser.

.....

..... [1]



- (d) (i) When 11.8 g of hydrated calcium nitrate(V),  $\text{Ca}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ , are gently heated, 3.6 g of water are lost, leaving the anhydrous salt,  $\text{Ca}(\text{NO}_3)_2$ .

Calculate the value of  $x$  in the formula of the hydrated salt.

$x =$  ..... [2]

- (ii) When anhydrous calcium nitrate(V) is heated more strongly, a brown gas and calcium oxide are some of the products.

Suggest an equation for this reaction, showing state symbols.

[3]

- (iii) Explain why calcium oxide has a high melting point.

.....  
.....  
.....  
..... [2]

(e) Calcium nitrate(V) is soluble in water.

- (i) Use the data below to calculate a value for  $\Delta S^\ominus_{\text{sys}}$  for the dissolving of anhydrous calcium nitrate(V).

Species	$S^\ominus / \text{J mol}^{-1} \text{K}^{-1}$
$\text{Ca}^{2+}(\text{aq})$	-53
$\text{NO}_3^-(\text{aq})$	+146
$\text{Ca}(\text{NO}_3)_2(\text{s})$	+193

$$\Delta S^\ominus_{\text{sys}} = \dots\dots\dots \text{J mol}^{-1} \text{K}^{-1} \quad [2]$$

- (ii) The standard enthalpy change of solution of anhydrous calcium nitrate(V) is  $-19 \text{ kJ mol}^{-1}$ .

Calculate the value of  $\Delta S^\ominus_{\text{tot}}$  for the dissolving of anhydrous calcium nitrate(V) at 298 K.

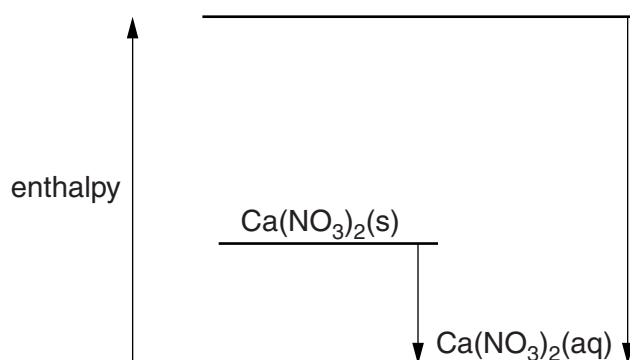
$$\Delta S^\ominus_{\text{tot}} = \dots\dots\dots \text{J mol}^{-1} \text{K}^{-1} \quad [2]$$

- (f) (i) Some enthalpy change data for the dissolving of anhydrous calcium nitrate(V) are given below.

		$\Delta H^\ominus / \text{kJ mol}^{-1}$
<b>A</b>	enthalpy change of solution of $\text{Ca}(\text{NO}_3)_2$	–19
<b>B</b>	enthalpy change of hydration of $\text{Ca}^{2+}$	–1650
<b>C</b>	enthalpy change of hydration of $\text{NO}_3^-$	–166

The energy level diagram that connects these quantities and the lattice enthalpy of  $\text{Ca}(\text{NO}_3)_2$  is shown in outline below.

- Label the top energy level with the correct formulae and state symbols.
- Label the arrows showing enthalpy changes. Use **letters** from the table above.
- Calculate a value for the lattice enthalpy.



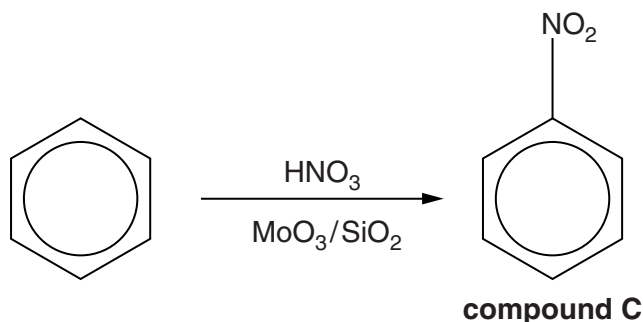
lattice enthalpy = .....  $\text{kJ mol}^{-1}$  [5]

- (ii) Name the forces between  $\text{Ca}^{2+}$  and water molecules in a hydrated calcium ion.

..... [1]

[Total: 25]

- 4 A 'green chemistry' method of nitrating benzene uses dilute nitric acid and a catalyst of  $\text{MoO}_3$  and  $\text{SiO}_2$  at  $140^\circ\text{C}$  to form compound **C**.



- (a) (i) Name compound **C**.

..... [1]

- (ii) Name the inorganic product of the reaction (apart from the catalysts).

..... [1]

- (iii) Give the systematic name for the ionic compound  $\text{MoO}_3$ .

..... [1]

- (b) 23.4 g of benzene produced 14.8 g of compound **C** by this method.

Calculate the percentage yield of compound **C**.

Give your answer to an **appropriate** number of significant figures.

percentage yield = ..... % [3]

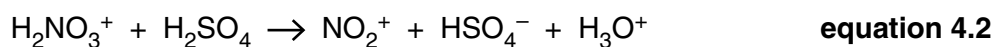
- (c) The 'traditional' method of nitrating benzene involves the use of concentrated nitric acid and concentrated sulfuric acid at around  $55^\circ\text{C}$ .

Suggest **one** way that the method using the  $\text{MoO}_3/\text{SiO}_2$  catalyst is **less** 'green' than the traditional method. Give your reasoning.

.....

..... [2]

- (d) When concentrated nitric acid and concentrated sulfuric acid are mixed together, they react as follows.



$\text{NO}_2^+$  acts as the nitrating agent in the reaction with benzene.

- (i) What is acting as the *base* in **equation 4.1**? Give a reason for your answer.

.....  
 ..... [1]

- (ii) Which is the stronger, sulfuric acid or nitric acid? Give a reason for your answer.

.....  
 ..... [1]

- (iii) Give the formulae of the conjugate acid–conjugate base pair in **equation 4.2**.

acid: ..... base: ..... [1]

- (iv) Nitric acid is a strong acid in aqueous solution.

Write an equation that shows this. Calculate the pH of a  $0.015 \text{ mol dm}^{-3}$  nitric acid solution.

equation:

calculation:

pH = ..... [2]

- (v)  $20 \text{ cm}^3$  of  $0.015 \text{ mol dm}^{-3}$   $\text{HNO}_3$  are mixed with  $10 \text{ cm}^3$  of  $0.015 \text{ mol dm}^{-3}$   $\text{NaOH}$ .

Calculate the pH of the resulting solution.

pH = ..... [2]

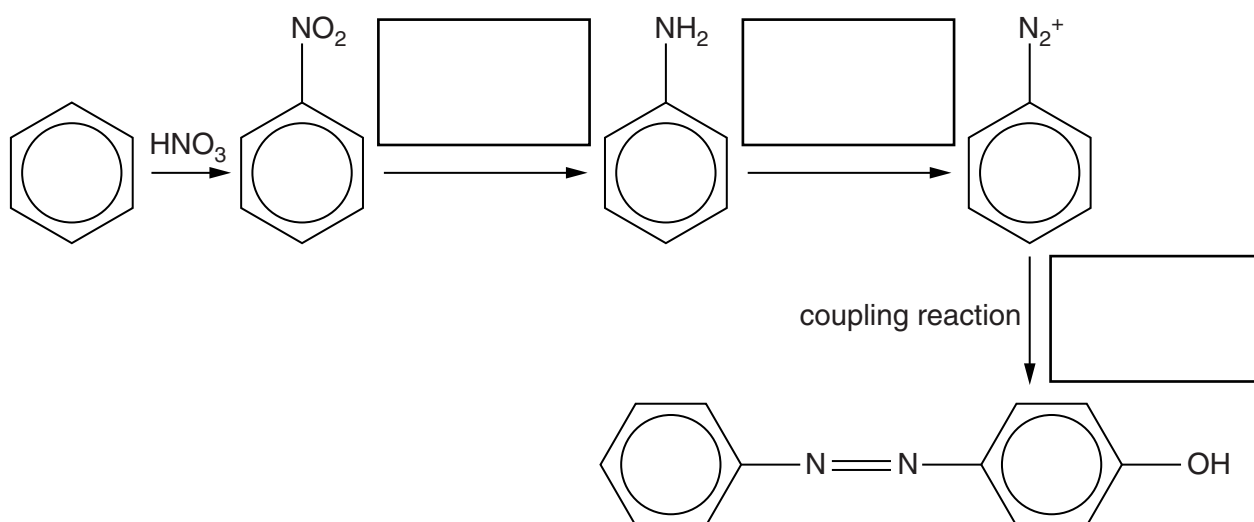
- (e) Explain the meaning of the circle in the centre of the benzene structure, giving the origin and arrangement of the electrons involved.



*In your answer you should use appropriate technical terms, spelled correctly.*

[4]

- (f) A synthetic route from benzene to an azo dye, starting with a nitration reaction, is shown below.



- (i) You may need to refer to your *Data Sheet* when answering this part.

Write, in the boxes by each arrow, the **reagents** used in the synthetic route above. [3]

- (ii) Give the **conditions** needed for the coupling reaction in the last step.

..... [2]



..... [6

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- 5 'Formaldehyde',  $\text{HCHO}$ , is a substance that has many uses as a preservative, a solvent and in making polymers.

(a) Draw the full structural formula for formaldehyde and give its systematic name.

formula

name ..... [2]

- (b) Formaldehyde can be made from methanol,  $\text{CH}_3\text{OH}$ . Formaldehyde is a gas at room temperature and methanol is a liquid.

Explain this difference in terms of intermolecular bonding.



*In your answer you should indicate how the points you make are linked to one another.*

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.....

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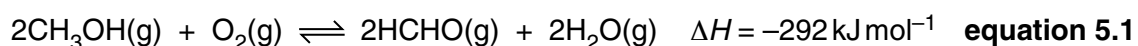
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.....

..... [4]

- (c) Formaldehyde can be made by oxidising methanol, using a catalyst. An equilibrium mixture is formed.



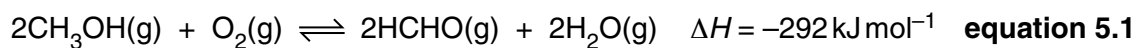
- (i) Complete the table below to show the effect of temperature, pressure and catalyst on the rate at which the equilibrium is achieved and the equilibrium yield of this reaction.

Use the words **increase** **decrease** or **no change**.

	<b>Increasing temperature</b>	<b>Increasing pressure</b>	<b>Adding catalyst</b>
<b>Rate</b>			
<b>Equilibrium yield</b>			

[3]





- (ii) The reaction in **equation 5.1** is carried out at 400 °C in an industrial process.

Using the information in your answer to (i), comment on the choice of this temperature.

.....  
 .....  
 ..... [1]

- (d) (i) Write the expression for the equilibrium constant for the reaction in **equation 5.1**.

[1]

- (ii) Give the effect, if any, on the value of the equilibrium constant of increasing the pressure and the temperature of the reaction.

pressure .....

temperature ..... [2]

- (e) Some reactions occur at all temperatures but others only occur above or below a specific temperature, as determined by entropy changes.

Will the forward reaction in **equation 5.1** occur at all temperatures or only above or below a specific temperature?

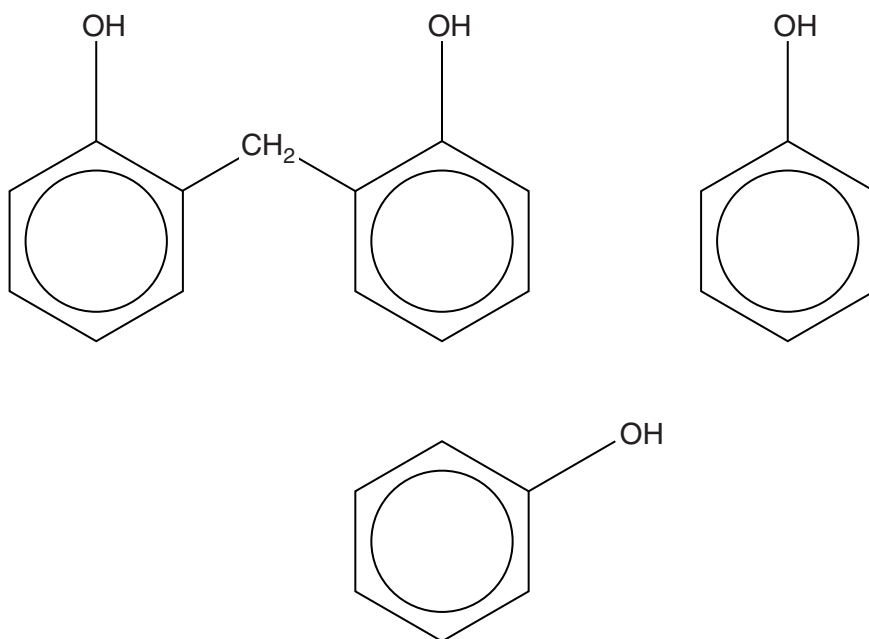
Explain your answer.

.....  
 .....  
 .....  
 .....  
 .....  
 .....  
 ..... [4]

**18**  
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**Question 5 continues on page 19**  
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- (f) A formaldehyde molecule,  $\text{HCHO}$ , can react with two phenol molecules to give the product shown below. This process can continue at the 2-, 4- and 6-positions on the phenol rings.



- (i) Extend the diagram above to illustrate links to the two further phenol molecules shown. [2]
- (ii) Classify the reaction that occurs when phenol reacts with formaldehyde as addition or condensation.

Give a reason for your answer.

.....  
 ..... [1]

- (iii) Describe the **structure type** of the final **three-dimensional** product.

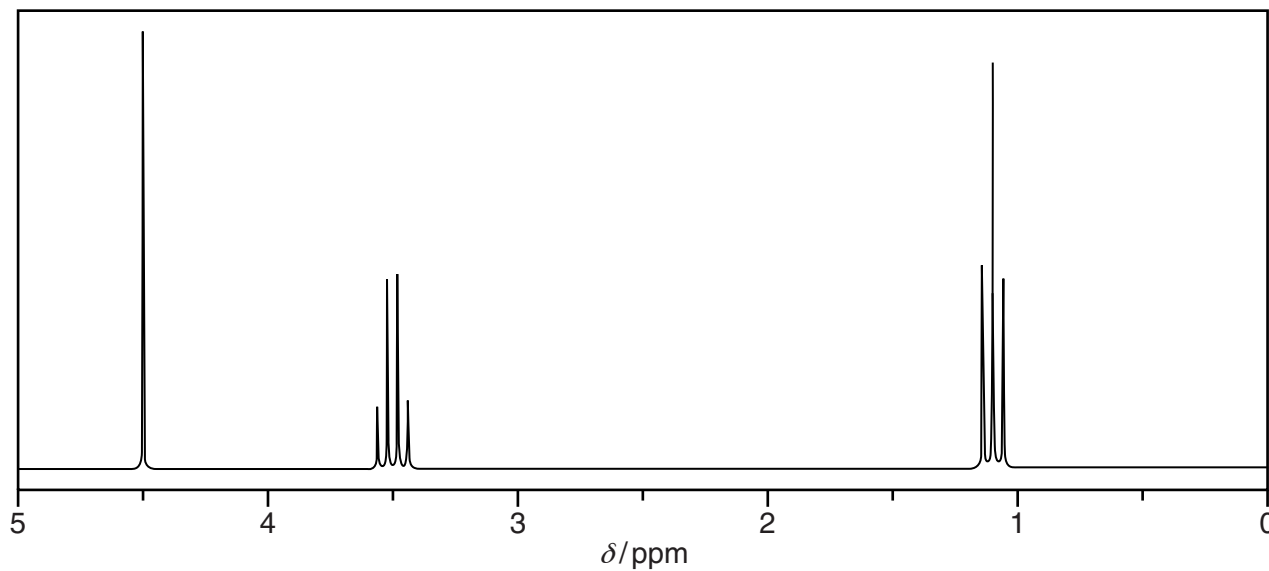
.....  
 ..... [1]

(g) A recommended replacement for formaldehyde as a solvent is compound **D**,  $\text{C}_5\text{H}_{12}\text{O}_2$ .

Spectroscopic data concerning compound **D** are given below.

*Infrared spectrum:* no peaks above  $1500\text{ cm}^{-1}$  apart from C–H.

*Proton NMR spectrum:*



You may use the rest of this page for rough working but ensure that you transfer all your answers to the spaces provided on page 21.

- (i) Explain why the lack of infrared peaks above  $1500\text{ cm}^{-1}$  (apart from C–H) means that compound **D** contains ether groups.

.....

.....

.....

.....

..... [3]

- (ii) Explain why the proton NMR spectrum indicates the presence of one or more  $\text{C}_2\text{H}_5$  groups in compound **D**.

.....

.....

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.....

..... [2]

- (iii) Give the structure of compound **D**,  $\text{C}_5\text{H}_{12}\text{O}_2$ , explaining how it matches the rest of the proton NMR spectrum.

.....

.....

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..... [2]

[Total: 28]

END OF QUESTION PAPER

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